

Cure Evaluation of Two Critical Composite Hybrid Flat Panels for use in a High-Dimensional Stability Satellite Application

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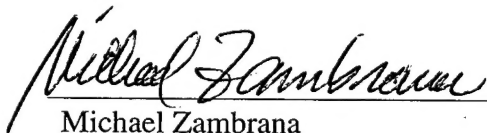
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14. ABSTRACT <p>Two large composite panels critical to a composite structure were recently fabricated. The panels consist of a complex hybrid of different fibers along with an ultra-low-moisture absorption siloxane-modified polycyanurate resin. After fabrication, the contractor noticed that the panels exhibited signs of partial cure by performing an acetone solvent wipe test. We were asked by the program office to assist the contractor in determining the extent of the contamination and whether the parts could be salvaged.</p> <p>Numerous composite tag samples were machined from the periphery of the part as well as moving inward from the edges. Dynamic mechanical analysis was performed on all samples to determine the extent of contamination. Our data suggested that severe carbamate formation had occurred in one of the panels. The suspected areas of the panel appeared compromised, as evidenced by a multimode loss modulus curve indicating several depressed glass-transition temperatures for the first panel. The second panel exhibited only minimal degradation. The contamination was primarily observed in the outer inch of the panel. The majority of the panel appeared well consolidated and cured. Machining the outer portions of the part salvaged the second panel. The other panel was too greatly compromised.</p>					
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1. Introduction

Recently, two large, thick composite hybrid panels were processed simultaneously in a large autoclave. The resultant parts were checked after cure, and a solvent wipe test performed by the contractor indicated that the parts did not appear to be fully cured. This was evidenced by residue left on the cloth believed to be from the matrix material. The resin used in the composites is a siloxane-modified polycyanurate system that is extremely susceptible to moisture contamination. We have written a number of reports^{1,2} discussing processing issues dealing with this material system and were asked to evaluate the state of the panels. Each of the panels is 51.0 in. x 24.0 in. The contractor removed small 2.0 x 1.0 in. sections from the north, south, east, and west portions of each panel. Figure 1 shows a schematic of one of these composite panels.

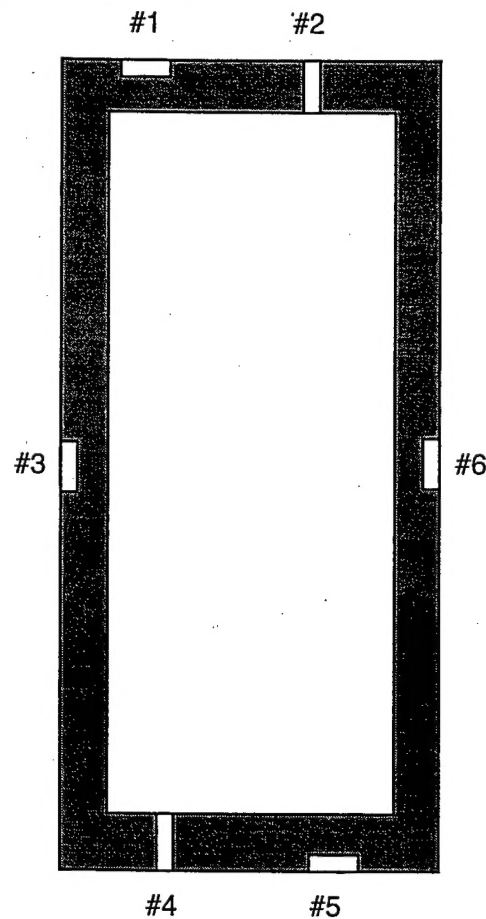


Figure 1. Schematic of composite panel tested in our investigation along with location of tag ends used for dynamic mechanical analysis testing. Gray area denotes problematic portion of laminate (window frame area) as evidenced by solvent wipe test.

The tag end samples were cut from the actual panels, as shown in Figure 1. The residue is believed to be concentrated on the outer 2 in. of the sample, similar to a window pane trace. Each of the tag end samples was tested using dynamic mechanical analysis (DMA). Each of the samples designated 1-6 was tested in two different modes. The entire thickness of the sample was tested, and only the outer few plies of specimens were also tested. Our previous studies have shown that contamination may be localized in the few outer plies, and measurements of Tg on the entire samples may be misleading unless severe degradation has occurred. Either way, if it is a surface effect or the entire sample has been affected, bonding onto this panel will make it prone to premature mechanical failure.

The objective of this report is to investigate portions of both panels and determine how the cure was compromised, how far into the panels the affected areas were, and, finally, whether the panels can be used as-is, or whether portions can be salvaged. The final question is dependent on structural mechanical data performed by the contractor.

2. Experimental

2.1 Dynamic Mechanical Analysis (DMA)

A Rheometrics Dynamic Mechanical Analyzer was used to determine the glass-transition temperature (T_g) of all composite samples. The DMA subjects a sample to cyclic torsional deformations and quantifies the material response by measuring the shear modulus, G' , the shear loss, G'' , and the lag angle between the applied stress and resulting strain, $\tan \delta$, as a function of temperature. In this report, the peak of the G'' curve was used for determination of the T_g values.

Numerous 2.0 x 1.0 inch tag end specimens were cut from the initial two large panels as shown in Figure 1. The tag ends were removed from the same areas in both panels. One half of the specimen was tested in the full thickness configuration, while the other was sanded down to the upper surface 20-mil thickness. Samples 1, 3, 5, and 6 were tested in two areas. The samples were further sliced along the longer dimension, leaving two 0.25 x 2.0 in. specimens from the outer edges. This was performed to identify whether any gradient in T_g exists through the thickness of the sample. Samples 2 and 4 were cut into three specimens moving along the longer 2.0-in. dimension (see Figure 2 for schematic).

2.2 Optical Microscopy

Transverse polished cross sections of the tested samples were prepared by mounting the sample in a room-temperature cured epoxy and grinding and polishing with diamond paste to a 1- μm finish. The cross sections were examined by optical microscopy with a Nikon Epiphot metallographic microscope equipped with a SONY DXC-107A CCD video camera.

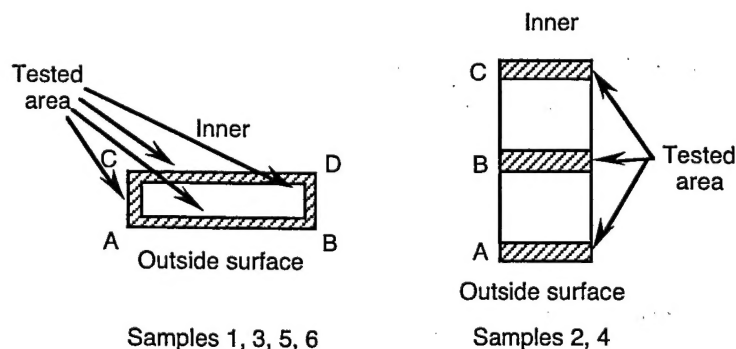


Figure 2. Schematic of tag ends prepared for dynamic mechanical testing. Hashed line region denotes sample area tested. Four segments are tested for samples 1, 3, 5 and 6. Three samples are obtained for samples 2 and 4. The longer dimension of each tag end is 2.0 in., and the shorter segment is 1.0 in.

2.3 Fourier Transform Infrared Spectroscopy (FTIR)

Microreflectance FTIR was performed using a Perkin Elmer 1310 Fourier Transform Infrared Spectrometer. FTIR was performed on both solvent-extracted residue and solid scrapings from the part. A detailed report discussing all of the variables used to quantify our test method is being prepared.

3. Results

Segments of both panels were investigated using FTIR spectroscopy. Scans indicated that contamination by hydrolysis was evidenced in both samples. Though the degree of hydrolysis could not be ascertained from FTIR, the mechanism was definitely related to carbamate formation. Dynamic mechanical analysis (DMA) of the parts to determine the T_g is better suited to evaluate the degree of contamination.

Figure 3 shows a DMA scan for panel 1. This scan shows the loss modulus as a function of temperature. Typically, the peak value for the loss modulus indicates the T_g. This material should produce a single loss modulus peak centered at about 170–175°C. As shown, the loss curve appears to be a combination of a number of peaks. This is usually an indication of severe hydrolysis contamination. As shown, there is a shoulder at 100, a peak at 125, and one at 165°C. This scan describes a resin system that is not only undercured but has regions cured to varying degrees. In other words, portions of the network have cured significantly while others are only slightly branched. Upon heat-treatment exposure, the lower crosslinked areas of the polymer are easily softened and cannot resist thermal degradation. Not only is this polymer system only partially cured, the hydrolysis of the system creates a more linear, less compliant matrix material that is different in chemical structure than what was intended. This DMA scan indicates serious moisture contamination. Additional heat treatments would have no effect on advancing the resin further or improving crosslinking density. Samples from this panel were placed in a solvent batch for a specific length of time as described in a previous publication.² The system was observed to completely dissolve within 5 min. Well-cured systems will not dissolve, even after exposure up to 5 h.

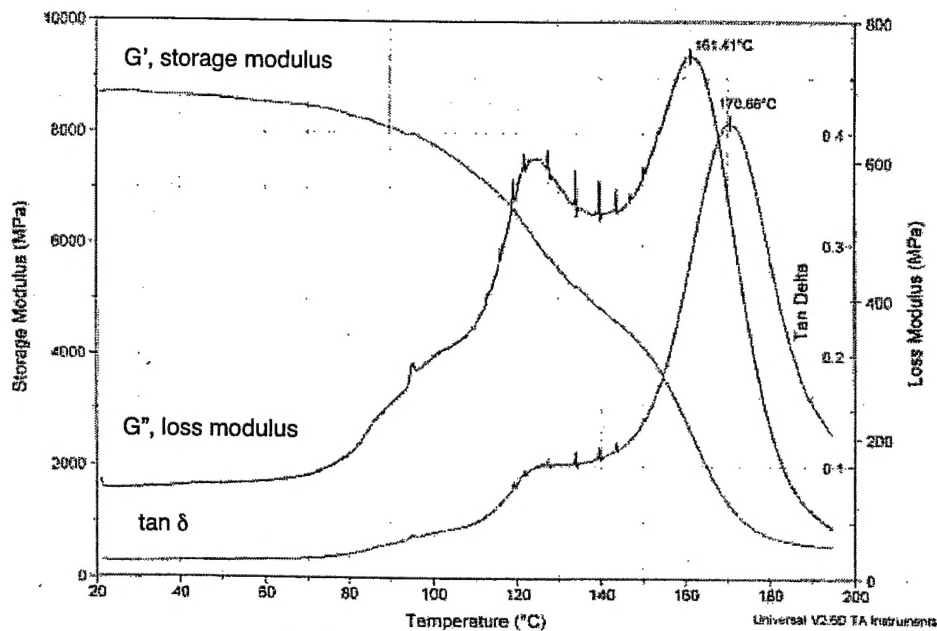


Figure 3. Typical DMA scan of Panel 1 on the outside edges.

Table 1 shows a compiled list describing the measured Tg values for the many tag end samples from Panel 1. As shown and described previously, there are a number of multiple Tg values for each tag end. This indicates severe moisture contamination. Samples 2 and 4 represent areas of the panel 0.05, 1.0, and 2.0 in. from the outer edge. The Tg values increase as the samples move in a few inches from the outer edges. However, even at a 2.0-in. depth, the resin still appears compromised. A Tg value of 165°C for this resin has been shown in previous publications to be both mechanically and thermally affected. Tag-end samples 3, 5, and 6 indicate changes in Tg values from the edge of the sample to 1.0 in. from the edge into the panel. Again, the values indicate an increase in Tg, showing improvement, but significantly lower than a well-cured material. The samples (1, 3, 5, and 6) tested laterally around the perimeter of panel 1 were shown to be quite consistent. The entire panel appeared to be hydrolyzed to the same degree on the outer sections. The Tg data for this panel shows that this composite was severely affected during cure. Mechanical flatwise tension tests are currently being performed, and the contractor has stated that preliminary data shows a higher-than-expected degree of scatter and low strengths. Once the resin becomes hydrolyzed during cure there is no remedy to obtain full cure. The by-products created during hydrolysis prevent a well-crosslinked, fully cured end product. Multiple peaks in the Tg curves for most tag ends led us to recommend scrapping the panel. Other issues, such as severe microcracking, thermal expansion coefficients, moisture absorption and thermal capabilities, will be affected.

Table 2 shows a compiled list describing the Tg values for the tag end samples from Panel 2. As shown and in contrast to panel 1, all of the samples for panel 2 had only one single sharp peak for the loss modulus. The DMA scan shown in Figure 3 shows this loss modulus peak, which represents the glass-transition temperature of the material. Samples 2 and 4 represent areas of the panel moving in from the outer edge. As shown, the Tg values show a slight increase in Tg as we move into the bulk of the panel. The slightly lower Tg on the outer perimeter may be due to some hydrolysis of the polymer. However, the Tg values are all quite high and above the values that

Table 1. Tg Data for the Tag End Specimens Taken From Panel 1

Sample Number	Through thickness	Width
1	Tg (a-b) = 110,125,161	Tg (a-c) = 110,125, 161
	Tg (c-d) = 110, 125, 165	Tg (b-d) = 110, 125, 161
2	Tg (a) = 125, 161	
	Tg (b) = 145, 161	
	Tg (c) = 165	
3	Tg (a-b) = 145,165	Tg (a-c) = 110,125, 161
	Tg (c-d) = 165	Tg (b-d) = 110, 125, 161
4	Tg (a) = 145, 161	
	Tg (b) = 155	
	Tg (c) = 165	
5	Tg (a-b) = 145, 161	Tg (a-c) = 110,125, 161
	Tg (c-d) = 165	Tg (b-d) = 110, 125, 161
6	Tg (a-b) = 145, 161	Tg (a-c) = 110,125, 161
	Tg (c-d) = 165	Tg (b-d) = 110, 125, 161

Table 2. Tg Data for the Tag End Specimens Taken From Panel 2.

Sample Number	Through thickness	Width
1	Tg (a-b) = 170	Tg (a-c) = 170
	Tg (c-d) = 170	Tg (b-d) = 171
2	Tg (a) = 169.9	
	Tg (b) = 170	
	Tg (c) = 170.9	
3	Tg (a-b) = 169	Tg (a-c) = 170
	Tg (c-d) = 170	Tg (b-d) = 169.9
4	Tg (a) = 170	
	Tg (b) = 172	
	Tg (c) = 172	
5	Tg (a-b) = 169	Tg (a-c) = 171
	Tg (c-d) = 170	Tg (b-d) = 171
6	Tg (a-b) = 170	Tg (a-c) = 170.7
	Tg (c-d) = 171	Tg (b-d) = 170.0

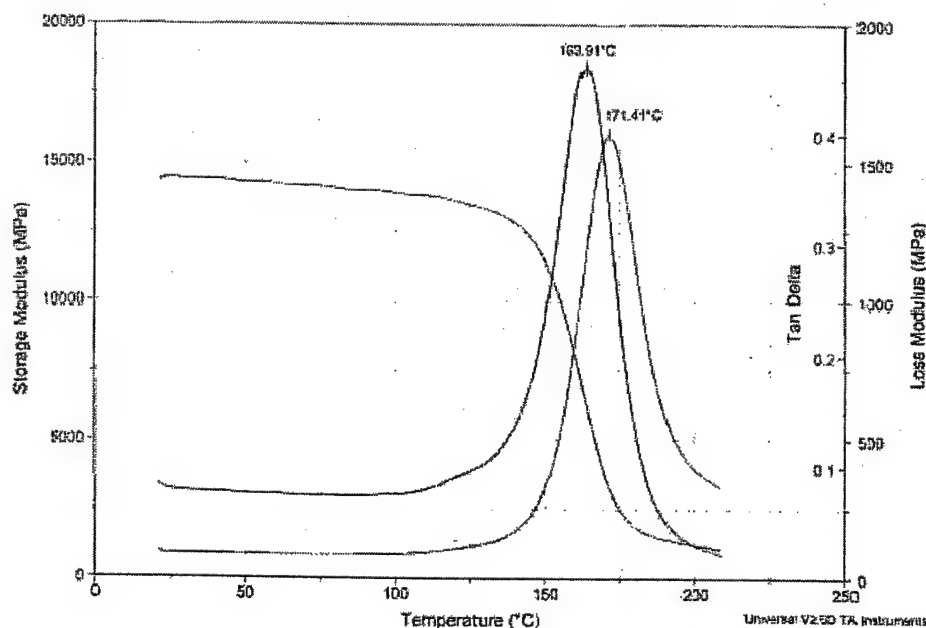


Figure 4. Typical DMA scan of Panel 2 on the outside edges.

are indicative of a well-cured system. The other Tg values taken from the tag ends around the perimeter of the panel indicate minimal changes and that full cure has occurred. The overall cure state of Panel 2 appears to be sound. It is quite surprising that the state of Panel 1 is so degraded in comparison to Panel 2 since both panels were processed simultaneously.

Fourier Transform Infrared (FTIR) spectroscopy was also performed to evaluate the degree of cure of the resin as well as to determine whether any contamination had occurred. Figure 5 shows a typical scan for the resin used in these composites as a function of heat-treatment temperature. There are

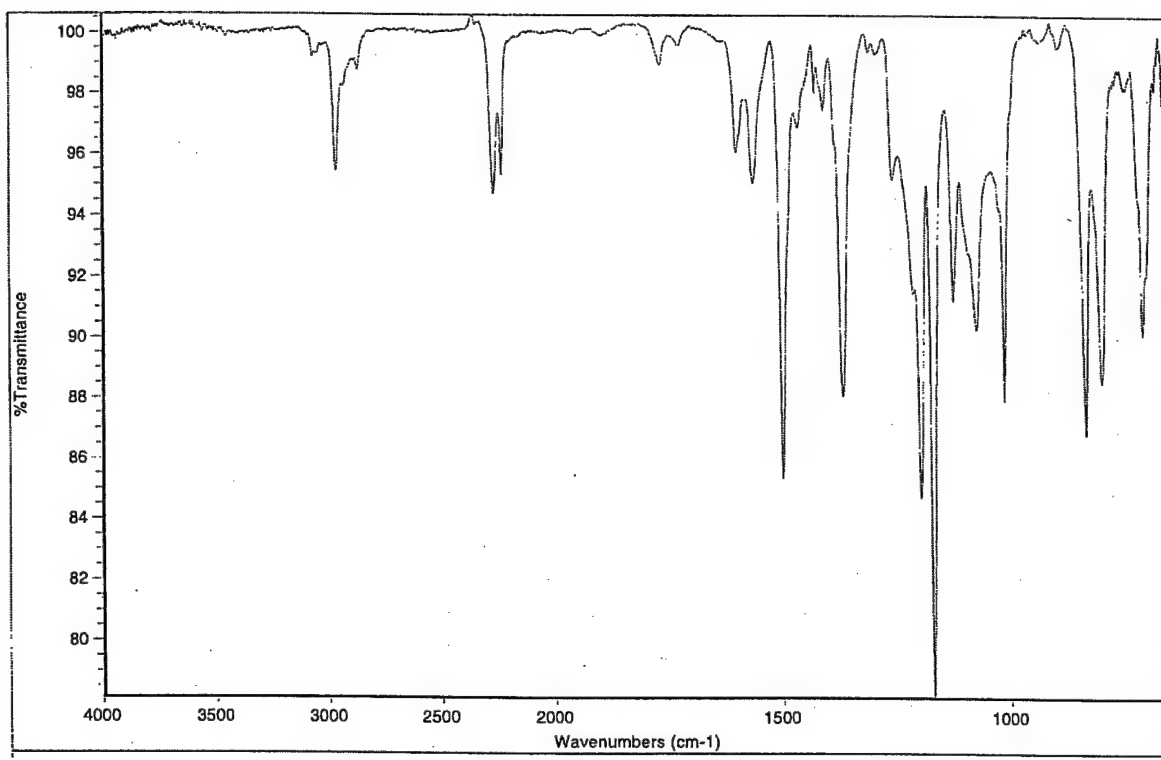


Figure 5. FTIR Spectra for typical siloxane modified cyanate ester resin.

three main areas of importance, as shown in the scans. The characteristic absorption bands of the cyanate ester groups are observed in the infrared spectrum between 2200 to 2300 cm^{-1} . The band is usually split into a doublet or triplet, depending on the chemical environment of the cyanate. Monitoring the disappearance of the cyanate ester absorbance bands can follow the polymerization of the resin. Even though this is generally a very good indicator of the degree of the initial stages of cure, identifying variations at higher degrees of cure is more difficult. A second set of peaks at 1560 and 1360 cm^{-1} reflects the absorption for the formation of the triazine ring as shown in Figure 6. The triazine ring is the primary polymerization route for this resin system. As this peak increases, the degree of cure increases; this is especially evident during the later stages of cure. Figure 6 shows an FTIR scan for the resin used in these composites as a function of the degree of cure. As shown from the figure, the polymerization can be followed quite readily for this system, especially at 1560 cm^{-1} .

The third peak to focus on is located at approximately 1750 cm^{-1} . This is a carbonyl peak that is usually indicative of hydrolysis of the cyanate ester occurring during the polymerization process. This type of carbamate contamination is the primary cause for large variations or decreases in the glass-transition temperature of the resin, even after heat treatment to high temperature. Figure 7 shows a typical FTIR with limited contamination.

In parts from both composite panels evaluated, the cyanate peak at 2250 cm^{-1} was completely consumed. This is typical in samples that are cured over 70% unless there has been moisture contamination. In those cases, the cyanate peak can be completely consumed due to hydrolysis with a limited degree of polymerization. The degree of cure was further evaluated, normalizing the peak located at

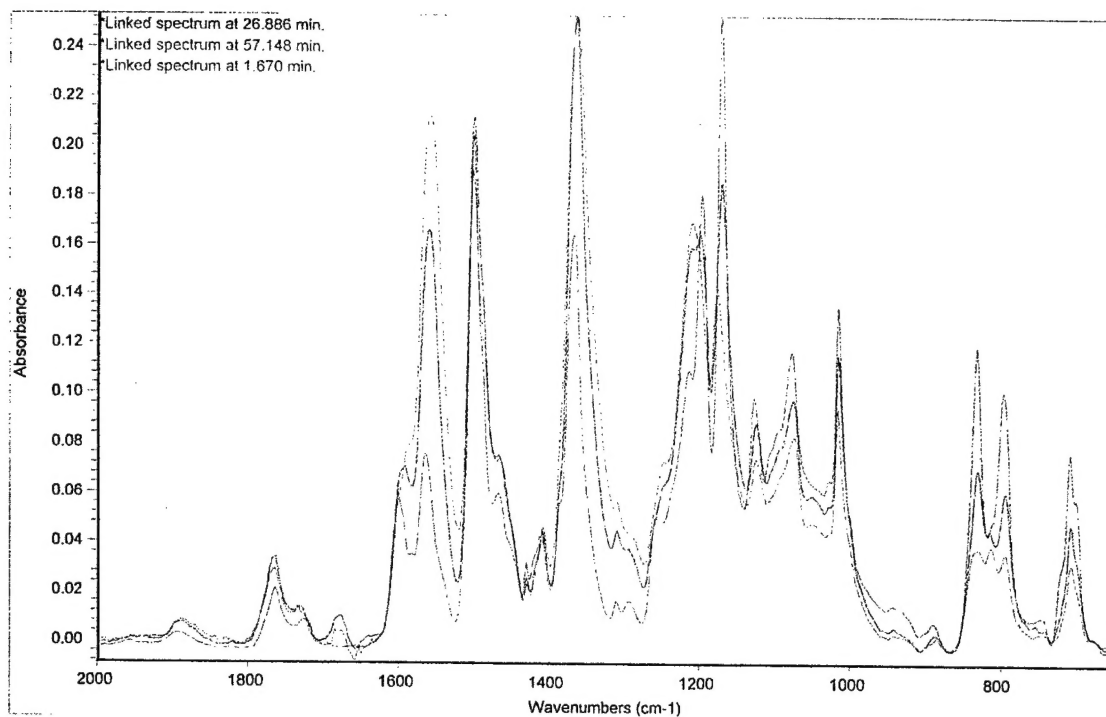


Figure 6. FTIR Spectra showing development of triazine ring formation during cure as indicated by peaks located at 1560 and 1360 cm^{-1} .

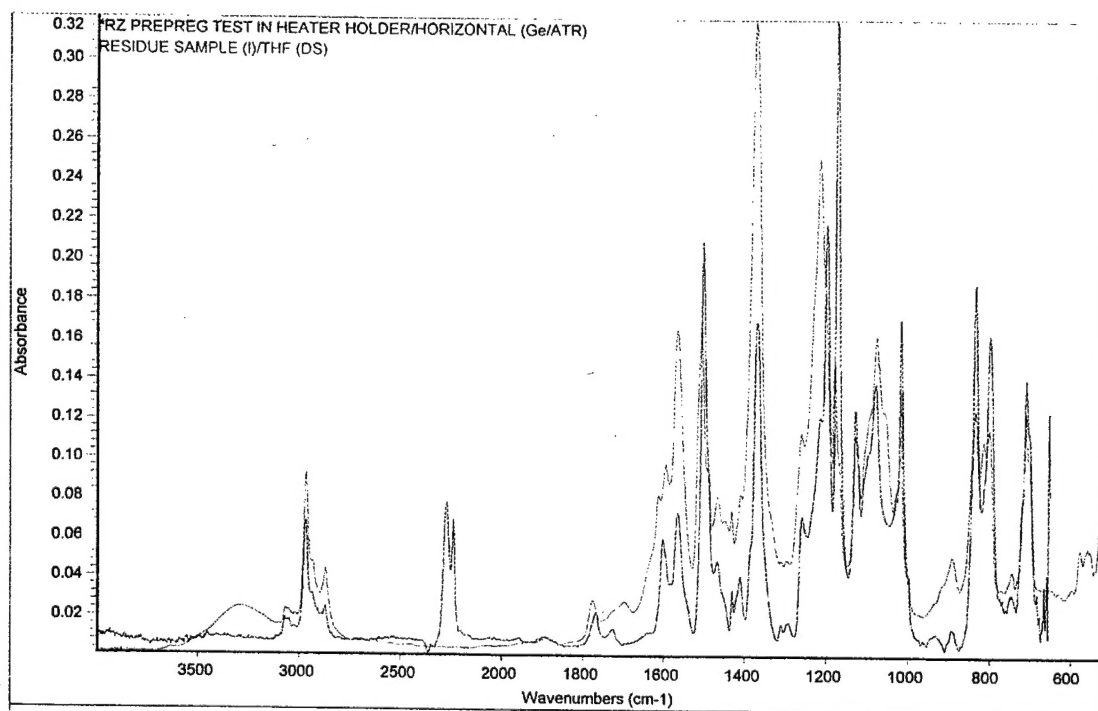


Figure 7. FTIR spectra showing indications of limited moisture contamination during cure. Blue spectra shows uncured system to emphasize differences in spectra.

1560 cm^{-1} for all parts taken from Panel 1 and Panel 2. Panel 2 appeared fully cured for all specimens and showed no evidence of hydrolysis contamination, which corroborates our measured Tg data. Panel 1, however, indicated a composite part that ranged in the degree of cure from 70 to 90%, depending on the location measured. The areas with the lowest degree of cure showed indications of carbamate formation. Even though by-products of hydrolysis were observed, the degree could not be easily quantified due to the convoluted nature of the peak.

At this time, we don't know whether both panels were fabricated using the same lots of material. Flatwise tension tests should still be performed to ensure that good consolidation of the panel has occurred; however, the cure state is satisfactory, and we see no reason to discard Panel 2. To assure highest reliability, Panel 2 should be machined 1.0 in. from the outer perimeter to remove any contaminated material.

4. Conclusions

- Samples from two large composite panels were tested using dynamic mechanical analysis (DMA) to evaluate their cure state. Solvent wipe tests by the contractor indicated partial cure of the resin used after final processing. Tag end segments were cut in areas suspected of partial cure and analyzed using FTIR, DMA, and solvent exposure tests.
- Panel 1 exhibited areas of severe hydrolysis that may have occurred during processing. Multiple peaks in the modulus curve indicated that the panel had areas with several glass-transition temperatures (Tg). Tg measurements of tag ends showed that the Tg of the panel increased as measurements were taken inward from the outer perimeter. However, the Tg values remained considerably below values indicative of full cure.
- Dynamic mechanical analysis of Panel 2 indicated that negligible contamination due to hydrolysis had occurred. The Tg values 1.0 in. in from the outer edge are representative of well-cured systems for this type of resin.
- We do not recommend using Panel 1 due to the severe degree of contamination that has occurred to the composite. Bonding to the surface of the composite may greatly affect mechanical performance. However, Panel 2 appears to be fairly well cured, especially 1.0 in. in from the outer perimeter. Panel 2 appears satisfactory for use with respect to its degree of cure. Additional, flatwise tension tests should be performed to evaluate variability and strength.

LABORATORY OPERATIONS

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